

High Energy Density Li-ion Cells for EV's Based on Novel, High Voltage Cathode Material Systems

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Project ID: # ES213

Overview

Timeline

- Start Date: December 2013
- End Date: December 2015
- No-cost extension to June 2016
- Percent Complete – 100%

Budget

- Total Project Funding: \$3,480,000
 - DOE Share: \$2,160,000
 - FFRDC: \$600,000
 - Contractor Share: \$720,000
- 2014 Funding: ~\$1,400,000
- 2015 Funding: ~\$1,780,000

Barriers

- Insufficient energy density of Li-ion battery systems for PHEV and EV applications.
- Insufficient cycle and calendar life of Li-ion battery systems.
- Accelerated energy loss at elevated voltages for Li-ion technology.

Partners

- Argonne National Laboratory:
 - Advanced Cathode Materials Development
- Lawrence Berkeley National Laboratory:
 - Advanced Cathode Materials Development
- DuPont:
 - High Voltage Electrolyte, Separator Development
- Nanosys/OneD Material, LLC:
 - High Capacity Anode Materials Development

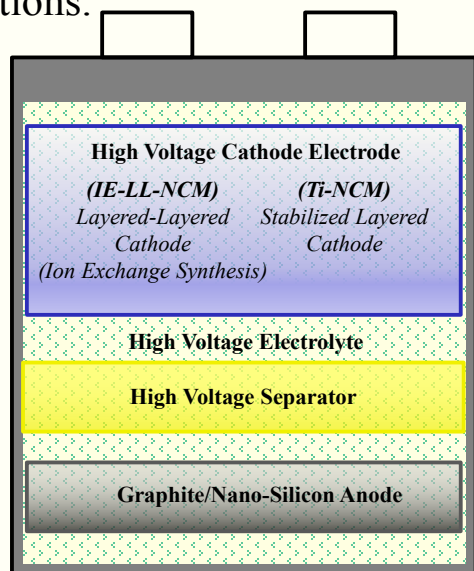
Relevance - Project Objectives

Project Goal:

The goal of this project is to develop and demonstrate new high energy, high voltage capable Li-ion materials and cell components to enable high energy, high power Li-ion cells that have the potential to meet the performance goals of PHEV40 and EV light-duty vehicles.

Performance Objective:

The objective is to demonstrate a PHEV40 cell with an energy density of 250 Wh/kg and an EV light duty cell with an energy density 350 Wh/kg that can meet the cycle life goals for those applications.



Cell Level Goals:

Energy Storage Requirements		PHEV40	EV
Characteristics	Unit		
Specific Discharge Pulse Power	W/kg	800	800
Discharge Pulse Power Density	W/l	1600	1200
Specific Regen Pulse Power	W/kg	430	400
Regen Pulse Power Density	W/l	860	600
Recharge Rate		C/3	C/3
Specific Energy	Wh/kg	200	400
Energy Density	Wh/l	400	600
Calendar Life	Year	10+	10
Cycle Life (at 30°C with C/3 charge and discharge rates)	Cycles	5,000	1,000
Operating Temperature Range	°C	-30 to +52	-30 to +65

Project Technical Targets

Year 1 (Gen 1):

Cell Level 230 Wh/kg, 1000 cycles (PHEV)

Year 2 (Final Deliverable Cells):

Cell Level 250 Wh/kg, 5000 cycles (PHEV), Cell Level 350 Wh/kg, 1000 cycles (EV)

Relevance - Technology

- New cathode and anode electrode materials and Li-ion cell components are required to enable major advances in the energy density of battery systems for transportation technologies.
- The layered and layered-layered “NMC” class of cathode materials paired against a silicon based anode offer the greatest potential to meet the PHEV and EV performance goals.
- Utilization of the inherent capacity in these systems can be greatly increased if higher voltage operation can be enabled.
- There are multiple interacting failure mechanisms at the materials and cell level that are barriers to achieving the system level battery performance goals.
- A focus on cell level development utilizing advanced materials and components is critical to achieving major breakthroughs in battery performance.

Second Year Technical Milestones

- Milestones leading to final deliverable cell build incorporating high-energy active materials, advanced electrolytes, and optimized cell designs:

FY2016 Milestones and Status

Milestone	Type	Description	Status
Selection of GEN 2 Cathode Materials	Technical	Physical and chemical characterization of Li-ion battery materials	Complete
Completion of GEN 2 Small Cell Testing	Technical	Projected Cell Performance Information, and Cell Test Plan	Complete
Provide Initial Testing Data and Deliver Cells to DOE	Technical	Test plan coordinated with the DOE and test cells delivered to directed site.	Complete

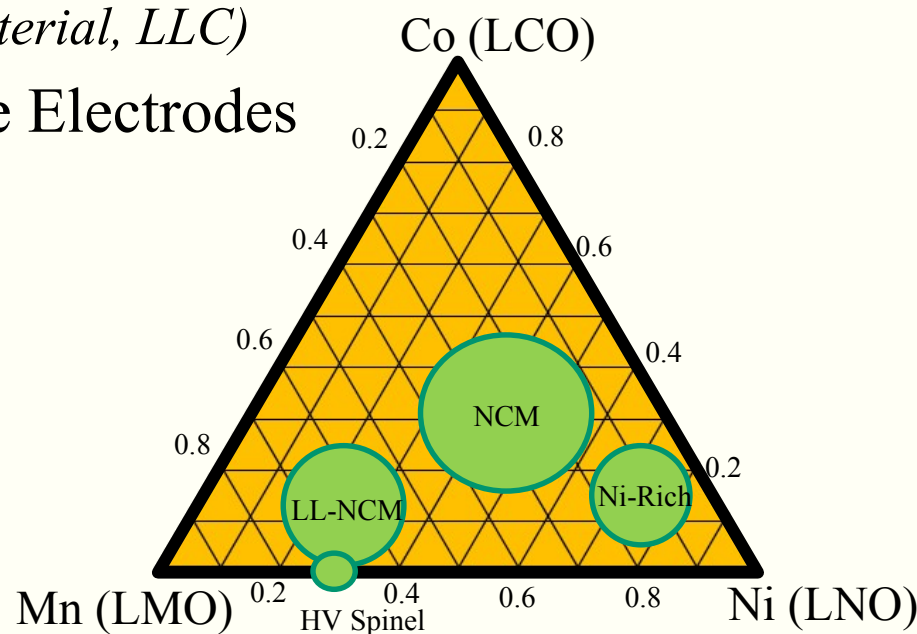
Project Progression:



Technical Approach

Development focused on addressing key current barriers to achieving high capacity long life Li-ion cells:

- Higher Capacity, Higher Voltage Active Materials
 - IE-LLS-NCM (*Argonne National Laboratory*)
 - Stabilized-NCM (*Lawrence Berkeley National Laboratory*)
 - Si-Graphite Composite (*OneD Material, LLC*)
- Higher Rate Capability Cathode Electrodes
 - Ion Exchange Synthesis
 - Composite Cathode Formulations
- Higher Voltage Operation
 - Cathode Surface Stabilization
 - Stable Electrolytes (*DuPont*)



Technical Approach

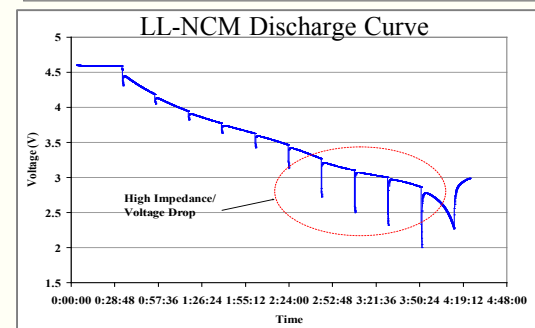
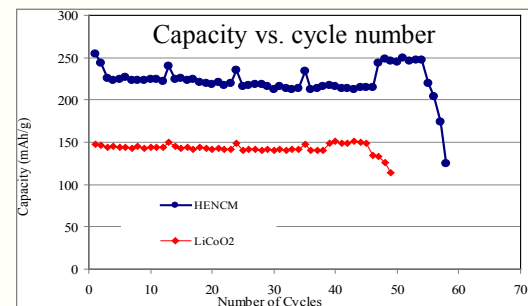
Ion-Exchanged “Layered-Layered-Spinel” NCM

Advantages:

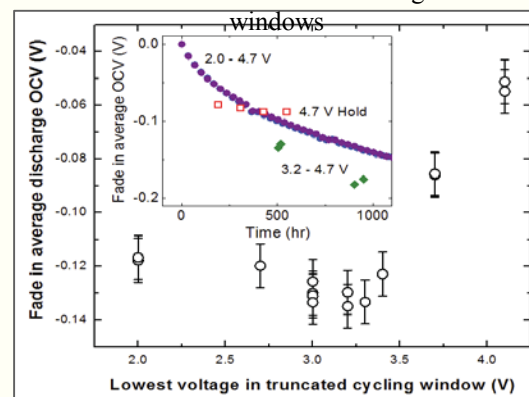
- High specific capacity – 230-250 mAh/g.
- Greater stability at high voltages.

Barriers:

- High impedance.
- State of charge dependent impedance and impedance growth.
- Voltage fade mechanism.
- Accelerated capacity loss if not stabilized.
- Low utilization in full cells.
- Low tap density.
- Wide voltage window.



OCV drop during cycling LL-NCM within different voltage

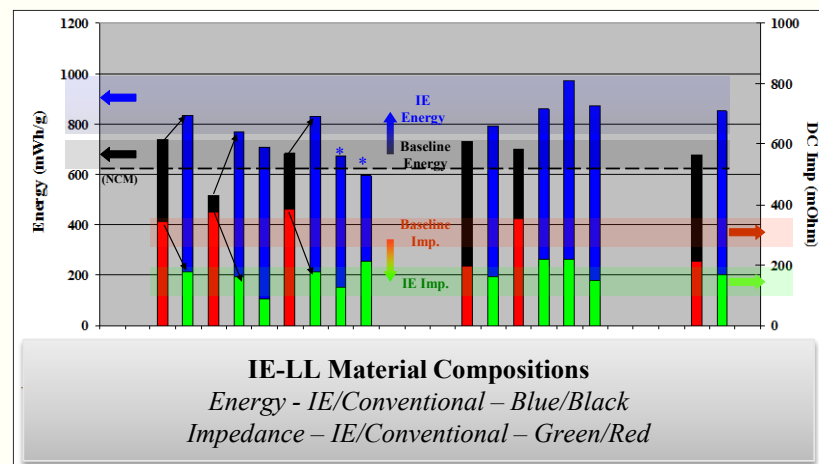


Technical Approach

Ion-Exchanged “Layered-Layered-Spinel” NCM

- Development strategy based on initial work done by Dr. Chris Johnson at Argonne National Laboratory and continued at Farasis Energy.
- Ion-Exchange Synthesis Approach
 - Na based LL-NCM material is used as a precursor to form Lithium LL-NCM through an ion-exchange process with Lithium (IE-LL-NCM)
 - Composition and synthetic conditions can be tuned to produce a high voltage spinel component to the LL materials → Layered-Layered-Spinel NCM (LLS-NCM)
 - Initial work indicates synthetic approach leads to materials with lower impedance and greater utilization.
- Potential for New Structural and Performance Characteristics
 - Potential to avoid O3 stacking and transition metal movement during cycling.
 - Route to creation of materials with larger interlayer spacings.
 - Route to introduce disorder into materials.
 - Route to materials with different surface morphology, stacking faults.

Comparison of energy and impedance measured for a number of IE and conventional LL-NCM compositions synthesized



Technical Approach

Layered NCM Materials

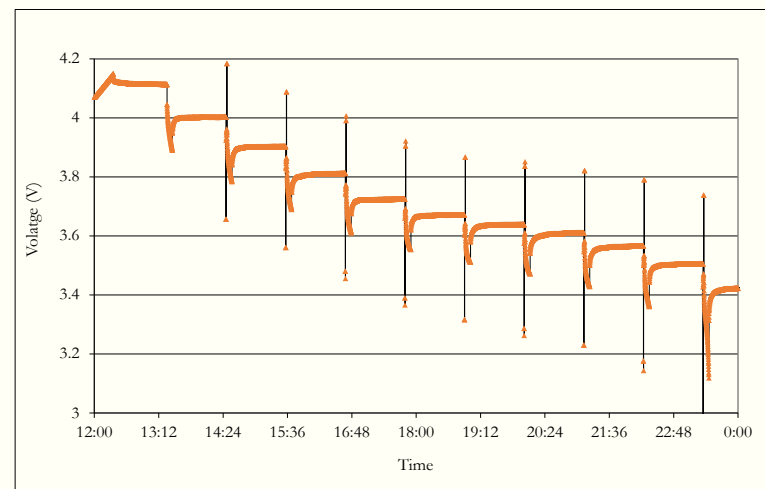
Advantages:

- Good rate capability
- High tap density
- Good stability at moderate voltages
- Reasonable average voltage

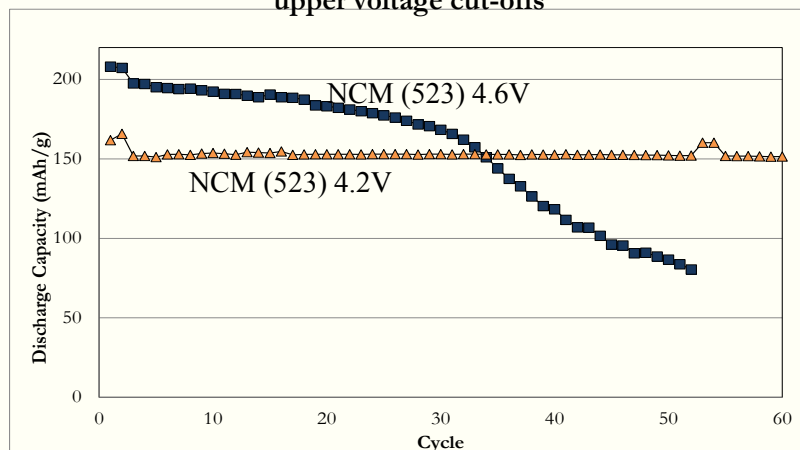
Barriers:

- Stability at high voltages.

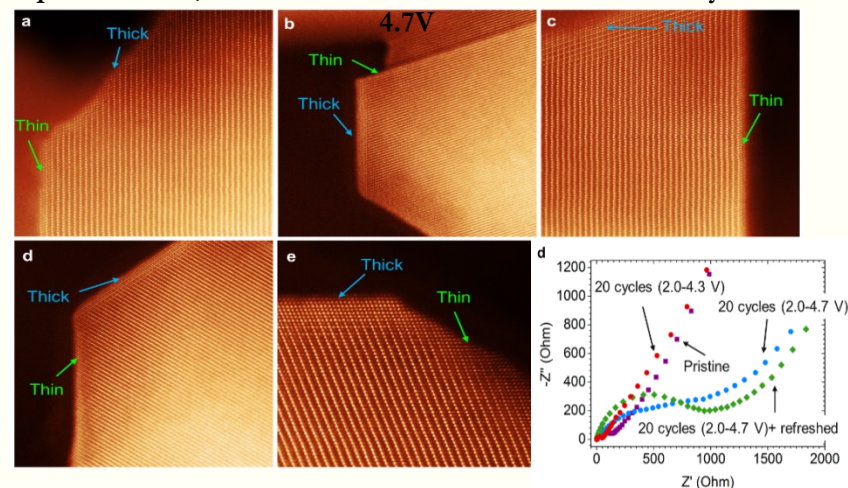
NCM/Graphite Cell HPPC test



Relative stability of NCM (523) cathode to different upper voltage cut-offs



Rock-salt surface reconstruction occurs upon electrolyte exposure alone, but is more severe when electrodes are cycled to



Technical Approach

Layered NCM Materials

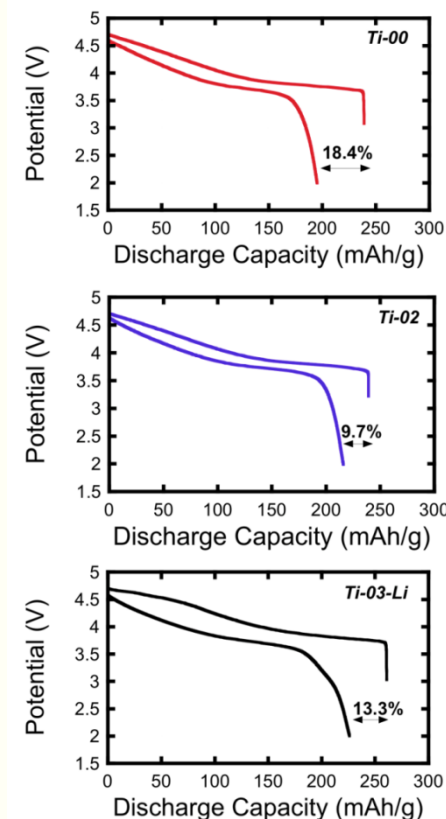
Surface Stabilization:

- Coatings/surface treatments.
- Decrease active material surface reactivity to electrolyte.

Doping:

- Bulk addition of elemental dopants to NCM composition.
- Stabilize layered structure in highly charged state.
- Aliovalent substitution to limit oxygen loss/surface reconstruction.

High Voltage Formation
Curves of Ti-Doped
NCM(424)



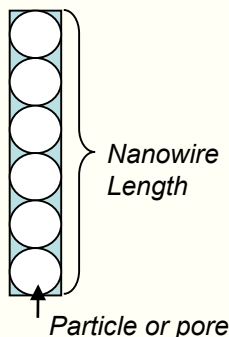
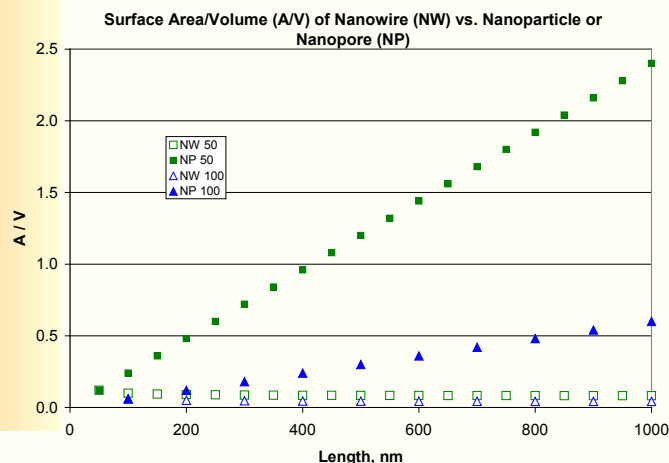
Kam, Kinson C., et. Al, J. Mater. Chem, 2011, 21 9991.

Technical Approach

Nano-Silicon Anode Materials

Nanosys SiNANode Approach vs. Hollow/Porous Approach

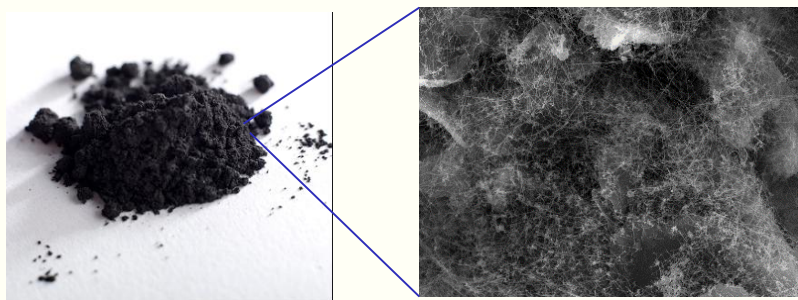
SiNANode	Hollow/Porous Si
Low A/V & Intact NW after cycling	High A/V; defects
Pack density similar to graphite	Pack density lower than graphite
Mass-produced with a competing cost * high Si utilization	Difficult and expensive to commercialize



- A Si nanowire is equivalent to several Si particles or pores with an identical diameter.
- Si nanowire has lower surface area/volume ratio (A/V) and hence less side-reaction with electrolyte and better cycle life

SiNANode production process: Directly grow Si nanowires on graphite powders

- Cost effective and high Si utilization
- Improves dispersion in slurry and drop in process (just replace graphite powders)
- Si-C conductivity improvement
- Si% or anode specific capacity is controllable, focusing on **500 ~ 1600 mAh/g**
- High electrode loading, as high as 1.5g/cm³
- Good cycling performance, cycled >1000 times



Technical Approach

High Voltage, High Energy Li-ion Cell

- Enable higher energy density cells by increasing the stability of the positive electrode at high voltage (> 4.4 V):
 - Stabilized active materials: NCM and LMR-NCM (collaboration with LBNL)
 - Fluorinated electrolytes (collaboration with DuPont)
- Enable higher power for LMR-NCM through novel synthesis methods
 - Ion-exchange layered-layered composite NCM (collaboration with ANL)
- Pair HV positive electrode technology with:
 - Graphite for higher power, longer cycle life PHEV cells.
 - Si/graphite composite (OneD Materials) for higher energy, lower cycle life EV cells.
- Overall approach and impact:
 - Lower costs for EVs by reducing number of cells needed to meet system targets and potentially simplifying packaging requirements.
 - Widespread adoption of EVs will significantly reduce GHG emissions.

Strategy - Development Plan

- Iterative Cycle - Lab Scale R&D with larger scale evaluation and development done in parallel.
- Three Generations of Cell Development leading to final deliverables:
 - Baseline – LL-NCM vs. Graphite (*baseline deliverable cells*)
 - Gen 0 – NCM vs. Graphite
 - Gen 1 – New Active Materials
 - Gen 2 – New Active Materials
- Cell level results and materials analysis inform next generation of materials development efforts.

Project Progression:

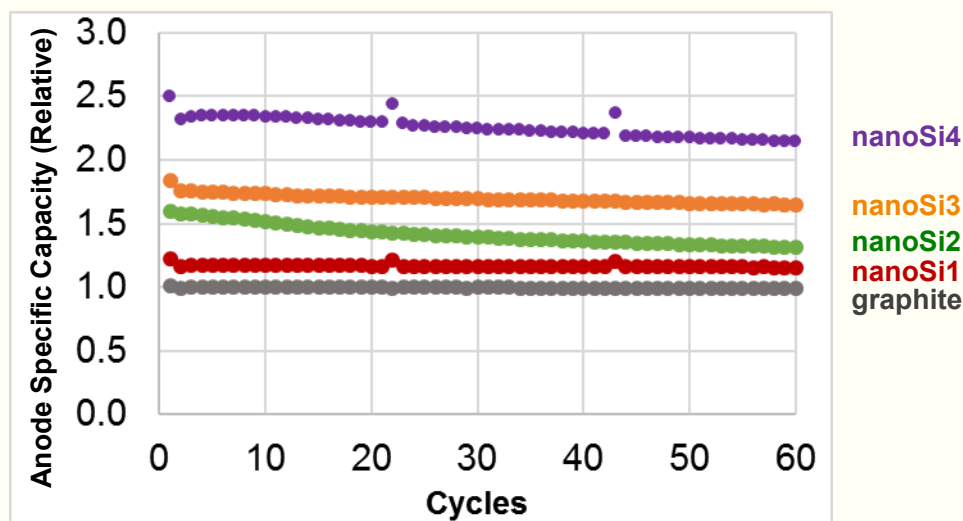
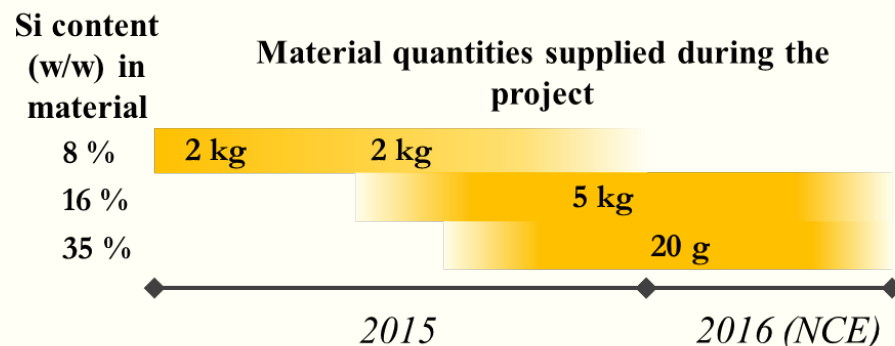


Technical Accomplishments

Silicon Negative Electrode

FY2015 effort focused on developing composite negative electrodes with higher Si content:

- Composite Electrode Formulation
 - Binders (CMC, CMC/SBR, PAN, PAA, ...)
 - Carbon additives (CF, graphene, carbon blacks)
- Positive Electrode Optimization
 - Active Material (NCM, LMR-NCM, blends)
 - Cell Balancing
- Electrolyte optimization
 - Solvents (various)
 - Additives (various)
- Cycling conditions
 - Formation conditions
 - Voltage windows
- **Negative electrode formulations with more than double the specific capacity of graphite were developed, enabling EV cell designs with specific energies >350 Wh/kg.**



Material evaluation in coin cells (*ca.* 6 mAh): Li metal negative electrode.

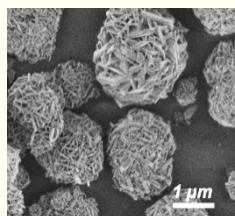
Technical Accomplishments

Ti-Substituted NCM

- Collaboration with Lawrence Berkeley National Laboratory (Marca Doeff).
- FY2015 effort consisted of evaluation of lower-cost alternate synthesis routes to Ti-NCMs by modifying commercial coprecipitated precursors and scale up of LBL's original coprecipitation process at Farasis.

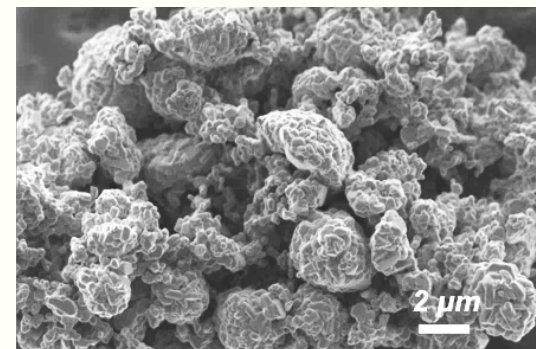
- X-ray spectroscopy indicates that using the new route, TiO_2 is not incorporated in the lattice but remains on the surface in an anatase-like environment. EDS shows that it is homogenously distributed on particle surfaces. Electrochemistry shows that it still imparts some benefit in high voltage stability.

$\text{M}(\text{OH})_2$ precursor

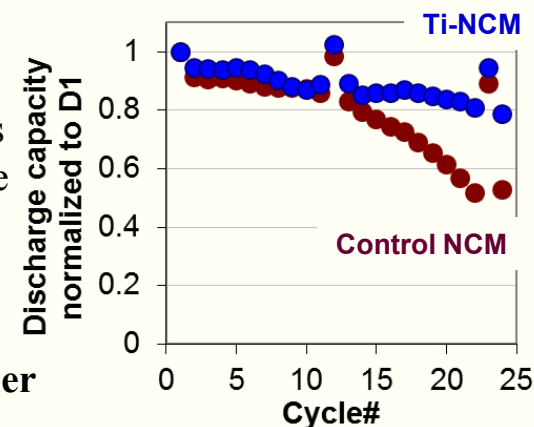


→
850 °C

+ TiO_2 (anatase) nanoparticles
+ Li source



- Farasis transferred LBNL's original coprecipitation route to 0.5 kg scale, incorporating Ti as TiOSO_4 in a separate feed to the reactor.
- **Ti-substituted material shows delayed onset of impedance growth and capacity fade under accelerated high voltage test conditions, reproducing the results from LBL.**

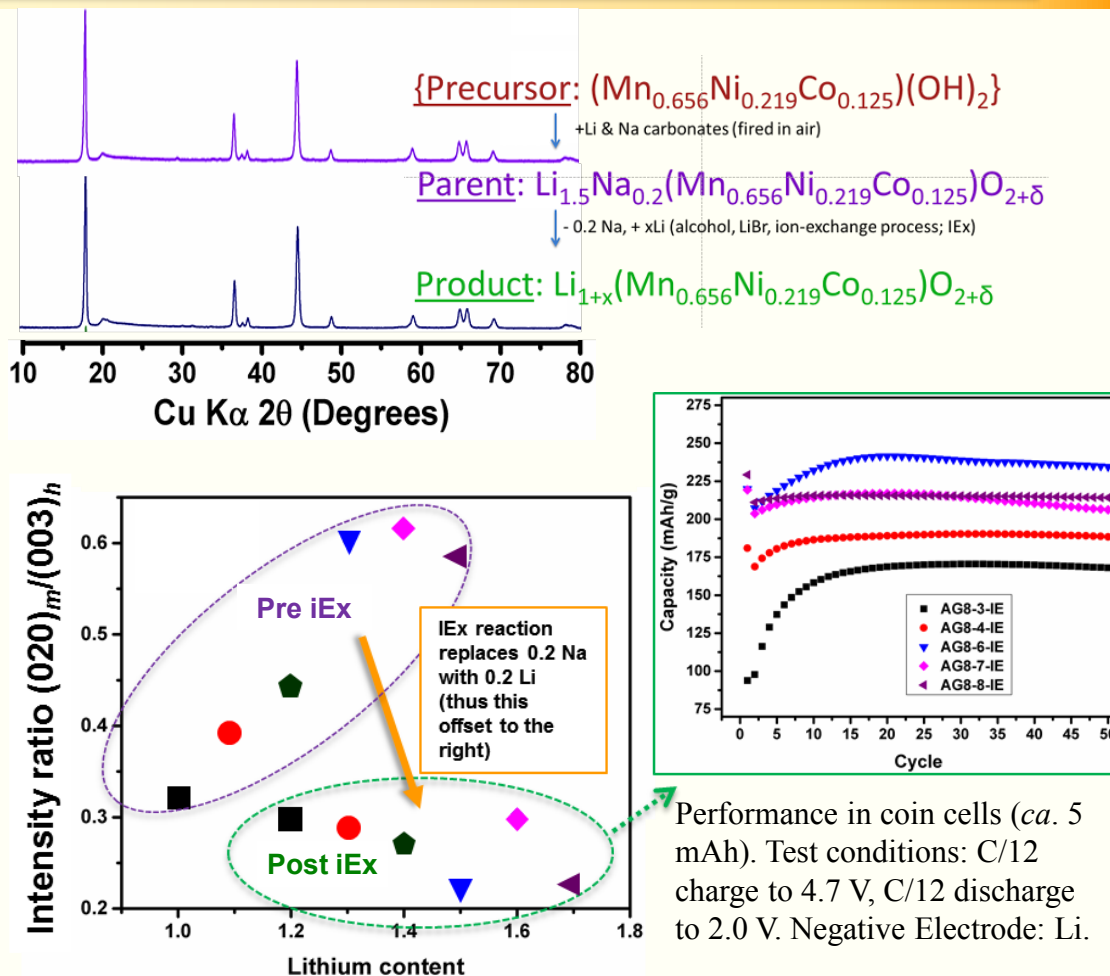


Performance in coin cells (*ca.* 6 mAh). Graphite Negative electrode. C/5 to 4.6 V, CV to C/50, C/2 to 2.5 V; 30 °C.

Technical Accomplishments

Ion-Exchanged LMR-NCM

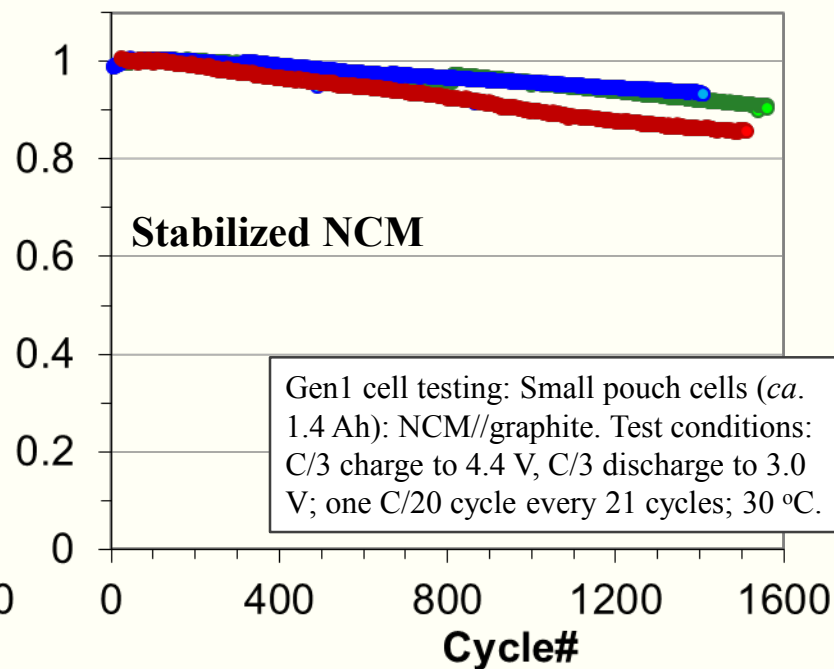
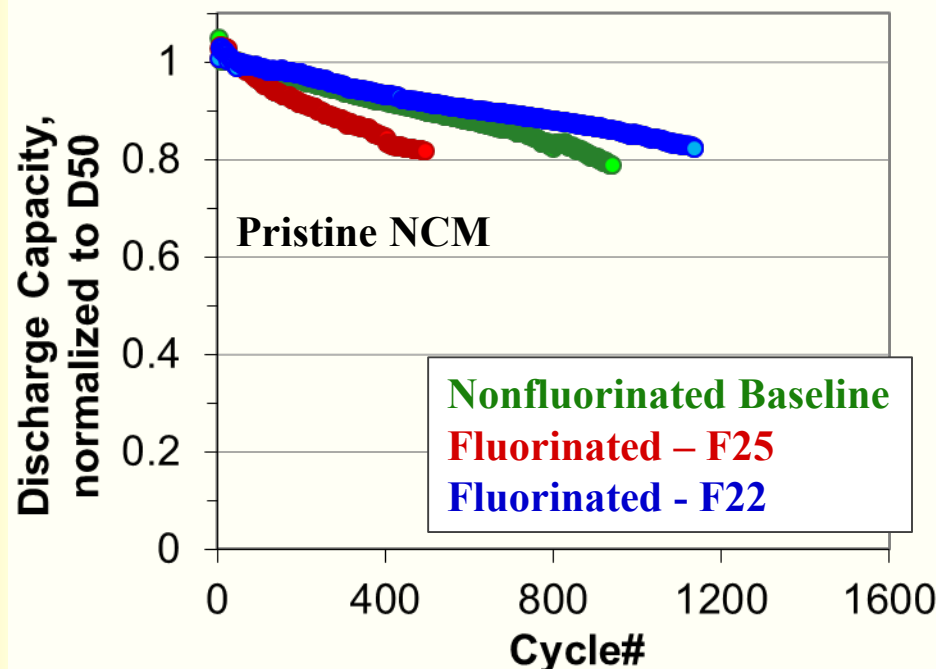
- Collaboration with Argonne National Laboratory (Chris Johnson).
- FY2015 effort focused on structural characterization of the best performing ion-exchange synthesized (iEx) materials and positive electrode formulations using LMR-NCM materials.
- **XRD pattern features that correlate with electrochemical performance were identified to help guide iEx synthesis.**
- **iEx-LMR-NCC materials with reversible capacities >220 mAh/g in a voltage window suitable for EV systems were identified, with improved power capability relative to conventional LMR-NCM.**
- Remaining barriers:
 - Cost of additional synthetic step (being addressed through cell chemistry modification to allow direct use).
 - Power capability still lags behind conventional NCMs (being addressed through positive electrode formulation).



Best performing samples have high $(020)_m/(003)_h$ ratios in the pre-iEx state. This ratio decreases post-iEx indicating that Li_2MnO_3 domains are affected by the structural disorder this process induces.

Technical Accomplishments

Gen1 Cell Build Ongoing Testing



- Some Gen1 cells, started in FY2014, are still on test (> 80 % initial capacity).
- Cells were also evaluated under accelerated failure testing conditions (higher temperatures, higher upper cutoff voltage, CV charging) and maintain the same relative capacity-retention ordering.
- Positive impact of fluorinated electrolyte is less prevalent in cells with stabilized NCM.
- **Fluorinated electrolytes can improve cycle life ...but can also lead to early failure.** In some cases this is due to gas generation.

Technical Accomplishments

Generation 2 Cell Build

PHEV Cell Design:	<i>ca. 2 Ah Small Pouch Cell (new format)</i>
Materials:	Stabilized HV NCM Graphite

EV Cell Design:	<i>ca. 250 mAh Small Pouch Cell (3-layer)</i>
Materials:	HV Stabilized NCMs/LMR-NCMs Graphite, 8% & 16 % SiNANode

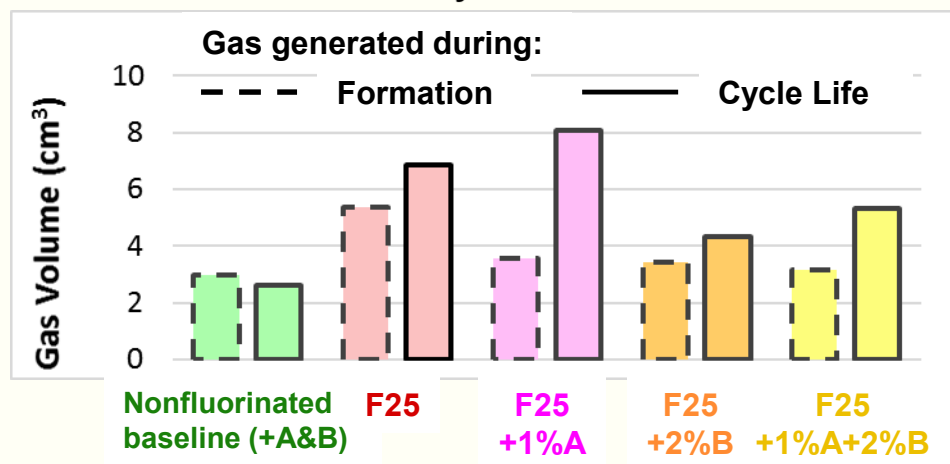
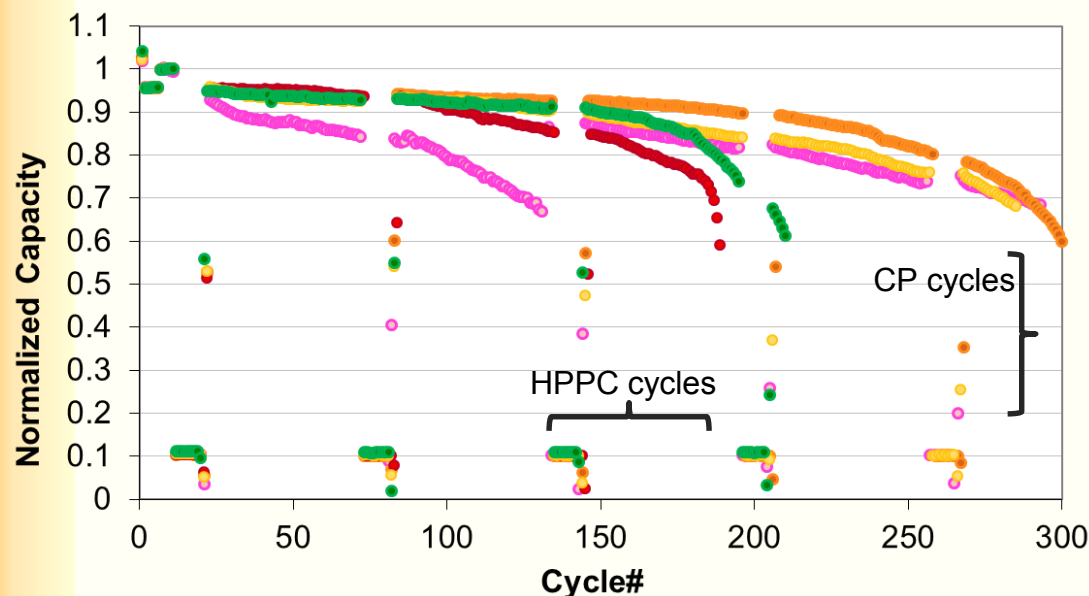
Electrolytes:	Baseline (LiPF_6 in EC/EMC) Multiple fluorinated solvent electrolytes Multiple additives
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Gen2 PHEV cell

- The Gen 2 PHEV cell was implemented in a redesigned form factor to increase actual energy density of small pouch cell.
- Extensive electrolyte screening was performed.
- Gen 2 EV cells were tested in smaller form factor due to material availability constraints of high Si content material.

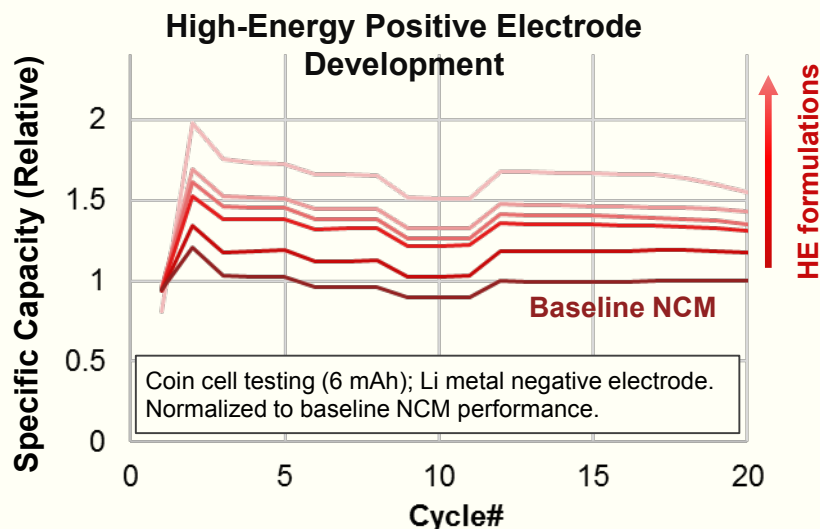
Technical Accomplishments: Gen2 PHEV Cell Electrolyte Development



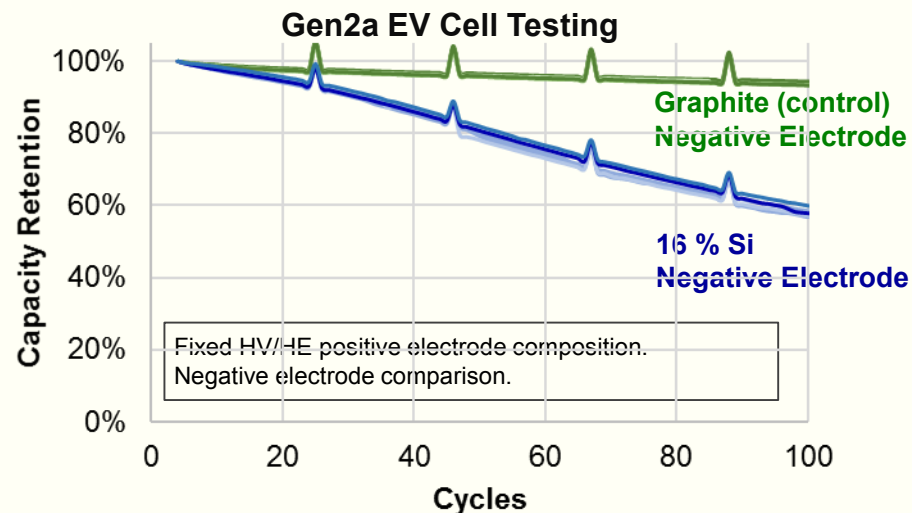
Gen2 PHEV accelerated testing cell performance: Small pouch cells (*ca.* 2 Ah); two cells of each design. Test conditions: C/2 CCCV charge to 4.5 V, C/100 cutoff, 1C discharge to 3.0 V; 30 °C. RPT consists of HPPC & CP measurements every 50 cycles.

- Electrolyte development in Gen 2 PHEV cell was conducted in 2 phases, screening different fluorinated solvent systems and additive packages.
- Using the same additive package, gas generated during formation is similar for non-fluorinated and fluorinated solvent systems, but *fluorinated electrolyte solvents tend to produce more gas during long term cycling.*
- The best fluorinated solvent systems extend cycle life by *ca.* 50% over nonfluorinated systems that use the same additives.

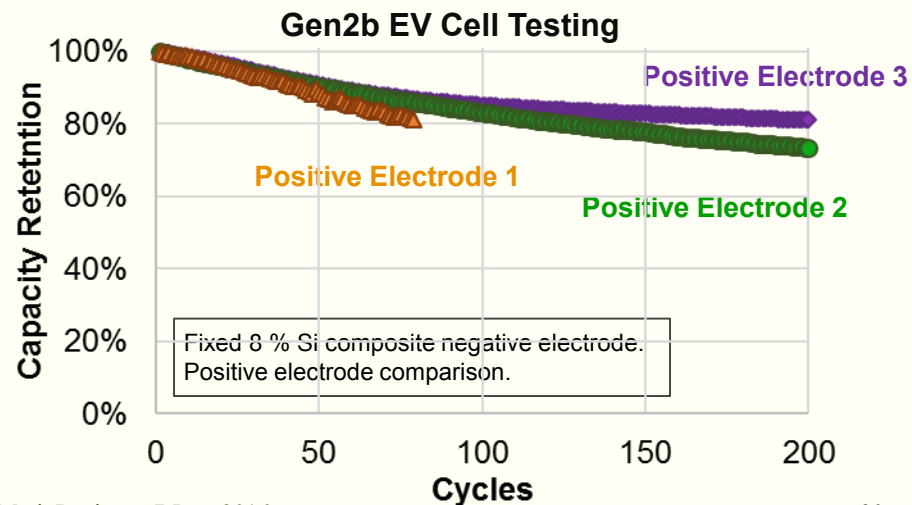
Technical Accomplishments: Gen2 EV Cell Development



- High Energy Positive Electrodes were developed with *useable* reversible capacities 1.2 – 1.4x that of a baseline NCM.
- Capacity fade in Si containing cells is largely due to continual SEI growth and electrolyte consumption.
- **High energy positive and negative electrode materials were integrated in the final EV deliverable build.**



Gen2 EV cell testing: Small pouch cells (*ca.* 250 mAh). Positive Electrodes: HV NCMs/LMR-NCMs.





Technical Accomplishments

Project Cell Build Summary

- Gen1 cell build explored diverse chemistry and provided experience to guide the Gen 2 cell build and testing.
- Gen2 cell build provided input for final refinements of deliverable PHEV and EV cell designs.
- EV cell design is still somewhat limited by poor cycle life of Si anodes.
- **Deliverable cell builds targeting PHEV and EV system performance goals utilized advanced positive and negative electrode active materials and fluorinated electrolytes developed in this program.**

Responses to Reviewer Comments

- In FY2015 project was reviewed favorably.
- Most poignant comments and our responses:

OVERALL
SILICON
ELECTROLYTE

Reviewer Comment	Response
“Overall approach is focused on energy; power / rate performance improvement needed as well.”	In general, energy targets are harder to meet. Experimental test protocols include impedance analysis (HPPC, EIS, etc.) to ensure sufficient power capability.
“... the anode side ... is focused on only one development route that has even lower scientific support [than the cathode strategy]. That route might be a small weakness” “It is recommended to intensify the work on [the Si anode part of the project]” “Cooperation could have been strengthened by including a partner for a second Si material source or detailed analysis.”	These projects are of limited scope by necessity. As suggested, Farasis intensified research on Si negative electrode technology in the second year through the end of the project.
“No information given regarding changes leading to improvements in electrolyte technology.”	We have included information regarding specific factors in electrolyte development.

Collaborations and Coordination with Other Institutions

Argonne National Laboratory (Chris Johnson, Eungje Lee, Arturo Gutierrez)

Federal Laboratory – Subcontractor providing materials and analytical work for project.

- Layered-Layered-(Spinel) (LL-S) NCM Cathode Material Development – Developing an ion-exchange synthetic approach to address the impedance and voltage fade barriers of high capacity LL-NCM cathode materials.

Lawrence Berkeley National Laboratory (Marca Doeff, Fen Lin):

Federal Laboratory – Subcontractor providing materials and analytical work for project.

- High Voltage Stabilized NCM Cathode Material Development – Develop and optimize doping and advanced coating methods to stabilize high capacity NCM materials to operation at high voltages.

Nanosys/OneD Material, LLC (Yimin Zhu):

Industry – Subcontractor providing materials and development guidance for project.

- Nano-Silicon Graphite Composite Anode Material Development – Optimize nano-silicon graphite composites for long term cycling stability.

DuPont (Srijanani Bhaskar):

Industry – Partner providing materials and analytical work for project.

- High Voltage Capable Electrolytes and Cell Components- Develop new fluorinated electrolyte systems, additives and separators with exceptional high voltage stability to advanced active materials.

Proposed Future Work

- **Project is complete.**
- **Continued Technology Development at Farasis.**
 - Increase Si content in negative electrode to push towards higher energy densities.
 - Continue electrolyte development for higher Si content electrodes.
 - Trickle down technology: Technologies developed in this project have been implemented in prototypes up to 10 Ah, targeting near term commercialization in niche markets.

Summary Slide

- Project goal is the development of high energy Li-ion cells capable of meeting the PHEV40 and EV performance goals set by DOE.
- Our approach to addressing current cell level performance barriers is based on advanced materials with a strong technical foundation.
 - **Improvements in capacity and rate capability were achieved for “layered-layered” cathode materials synthesized via the ion-exchange synthetic route.**
 - **Bulk-doping of NCM materials with Ti improves stability when cycling at high voltage.**
 - **Novel high voltage electrolytes improve long term high voltage operation.**
- Strong coordination with subcontractors and partners has allowed parallel development of multiple cell components and incorporation into high performance cells.
- The final phase of the project focused on final optimizations of deliverables.
- **The project has significantly advanced the TRL for these technologies.**